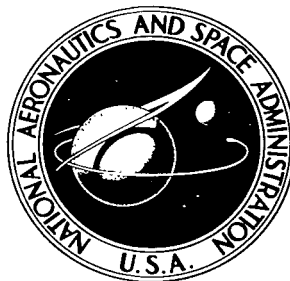


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ON RATE OF BURNING
(DECOMPOSITION WITH FLAME)
OF LIQUID HYDRAZINE

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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EFFECT OF PRESSURE ON RATE OF BURNING (DECOMPOSITION WITH FLAME) OF LIQUID HYDRAZINE

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SUMMARY

Measurements of flame properties were made for liquid hydrazine burning (decomposing with flame) in narrow glass tubes (5.6-, 9.5-, and 12.7-mm diam.; 10 by 10 mm square). They included temperature and light emission from the flame; color photographs were taken. The observations were all made between 1 and 18 atmospheres under a nitrogen atmosphere.

The results support the postulate that the rate of propagation of the burning process is controlled primarily by a second-order gas-phase reaction rate, and that the observed variation from linearity in the burning rate - pressure curve is due mainly to physical factors rather than to a change in the course of the overall reaction. Relations are seen between the size and shape of the flame and the burning rates. The reasons for the abrupt breaks in the burning rate - pressure curves are not clear, but the pressure variation is similar to those of extinction and quenching.

INTRODUCTION

Various interpretations have been made of the effect of pressure on the rate of consumption of liquid hydrazine burning in glass tubes (refs. 1, 2, and 3). It was concluded in reference 1 that the burning rate (liquid consumption rate) was controlled primarily by a second-order gas-phase reaction rate, but was limited at lower pressures by an evaporation rate.

It was also found in reference 1 that there were abrupt increases in the burning rate as pressure was increased. For example, in a typical series of experiments with 100.0 percent hydrazine in a 5.6-millimeter tube, there was a regular and relatively slow increase in rate as the pressure increased from 1 to about 12 or 14 atmospheres. At about 14 atmospheres the rate increased so rapidly that replicate determinations at apparently the same pressure gave nearly a two-fold range in rates for an experiment which was otherwise reproducible to within 10 percent. At pressures above 14 atmos-

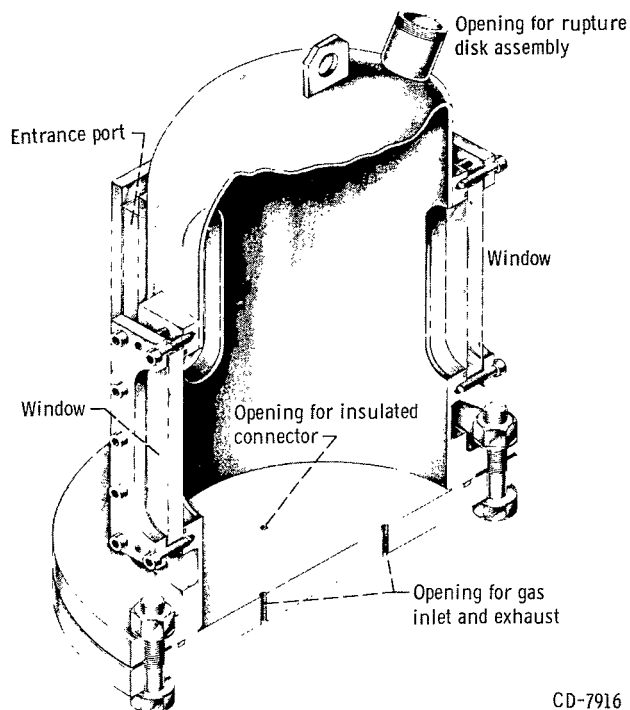


Figure 1. - Strand burner.

phers the rate continued to increase from the highest value previously determined in a regular manner. The pressure at which these "breaks" in rate occurred varied with tube size and hydrazine concentration. The breaks in the curves were not accompanied by a change in the smoothness of burning, or any other readily visible distinguishing feature as is sometimes observed in other systems (refs. 4 and 5). It was supposed in reference 1 that, barring a change in chemical mechanisms, the behavior observed was hydrodynamic in origin.

The purpose of this research was to examine the decomposition process in more detail with a view to determine what chemical or physical changes may be occurring that limit the rate and

cause the abrupt break in the burning rate - pressure curve. Consequently, measurements were made of the flame temperature and of the light and sound emission; in addition, color photographs were made of the decomposition flame.

EXPERIMENTAL APPARATUS AND PROCEDURE

The strand burner used is shown in figure 1. The body of the burner is made from a 12-inch-diameter stainless-steel pipe with a welded pipe cap. Two windows of about 2 by 8 inches are set 180° apart; a third window opening serves as an entrance port to the chamber. This third window is closed by bolting a steel plate over the opening. A base is bolted to the flange of the body. It contains openings for inlet and exhaust of the pressurizing gas and a high-pressure insulated connector for bringing through thermocouple leads and igniter wires.

Figure 2 shows the apparatus used for the burning rate measurements. A Nichrome wire coil placed at the surface of the liquid served as the igniter. The chamber was purged with nitrogen gas to free it of air before the liquid was ignited.

The rate of regression of the surface was measured by photographing the receding surface. The usual procedure was to illuminate the sample, place horizontal markers

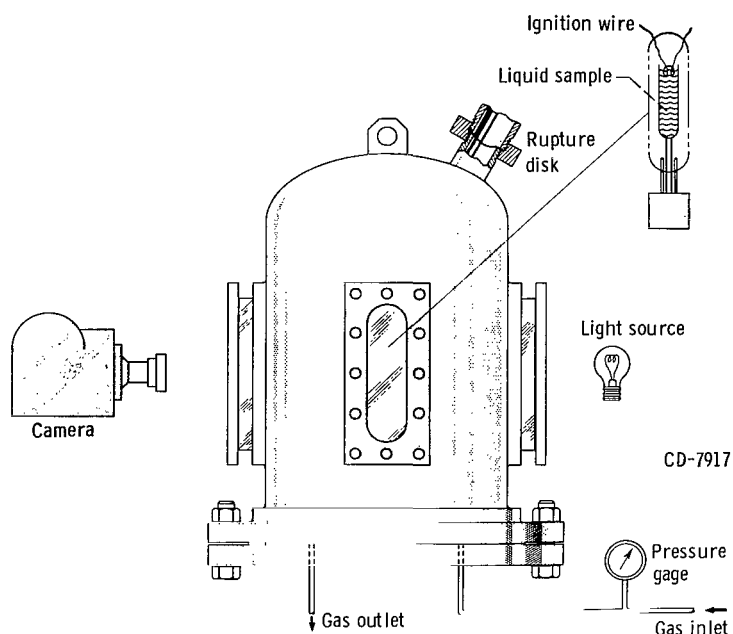


Figure 2. - Experimental apparatus used for burning rate measurements.

2 centimeters apart, and obtain the rate using a camera speed of 24 frames per second. Color photographs of the flame were made by darkening the chamber and photographing at 8 frames per second.

For measuring flame temperatures, a platinum - platinum rhodium (10 percent) thermocouple of 0.0004-inch diameter (<0.001 -in. junction) was threaded horizontally through the tube. The couple was cemented firmly in place with the junction located as closely as possible in the center of the tube. The output of the thermocouple was recorded on an oscillograph.

Measurements of the amount of the visible and near ultraviolet light emitted were made by focusing the collimated output of the flame onto a 1P28 multiplier phototube and by measuring its output on a cathode ray oscilloscope. Measurement of the sound emitted during the burning was made by suspending a BR-180 condenser microphone about 1 inch above the tube. The output of the microphone was amplified and recorded on magnetic tape.

The measurements and observations of hydrazine burning were made between 1 and 18 atmospheres of pressure. The glass tubes used were 5.6, 9.5, and 12.7 millimeters in diameter and 10 by 10 millimeters square.

Technical hydrazine containing better than 95 percent hydrazine by weight was dried over calcium hydride for 3 hours in a dry nitrogen atmosphere and then vacuum distilled. Analysis by an iodate method showed the material to be 99.9 percent concentration or better.

TABLE I. - MAXIMUM

GAS TEMPERATURE

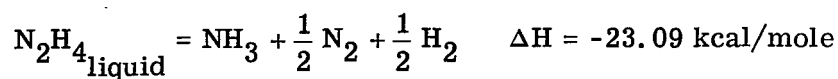
Pressure, atm	Maximum gas temperature, °K	Linear burning rate, cm/sec
1	1400	0.026
	1390	-----
	1375	-----
	1390	-----
10	1375	0.086
12	1400	0.087
	1345	.091
	1335	.088
	1395	.096
	1415	.090
14	1425	0.135
	1380	.174
	1340	.110
	1380	.090

TABLE II. - AMOUNT OF
EMISSION OF VISIBLE
LIGHT FROM FLAME

Pressure, atm	Relative amount	Linear burning rate, cm/sec
1	1.00	0.026
4	.81	.052
6	.59	.061
10	.62	.080
12	.64	.085
14	1.05	.180
16	1.14	.197

RESULTS AND DISCUSSION

The equation for the homogeneous decomposition with flame is believed to be



and gives a calculated flame temperature of 1480° K using heat capacity data from reference 6. Analyses of the combustion products have been made (refs. 7 and 8) which show that this equation is approximately correct at pressures of 1 atmosphere and below, both in gaseous and liquid burning systems. Data obtained by Adams and Stocks (ref. 2) for liquid burning above 1 atmosphere did not in-

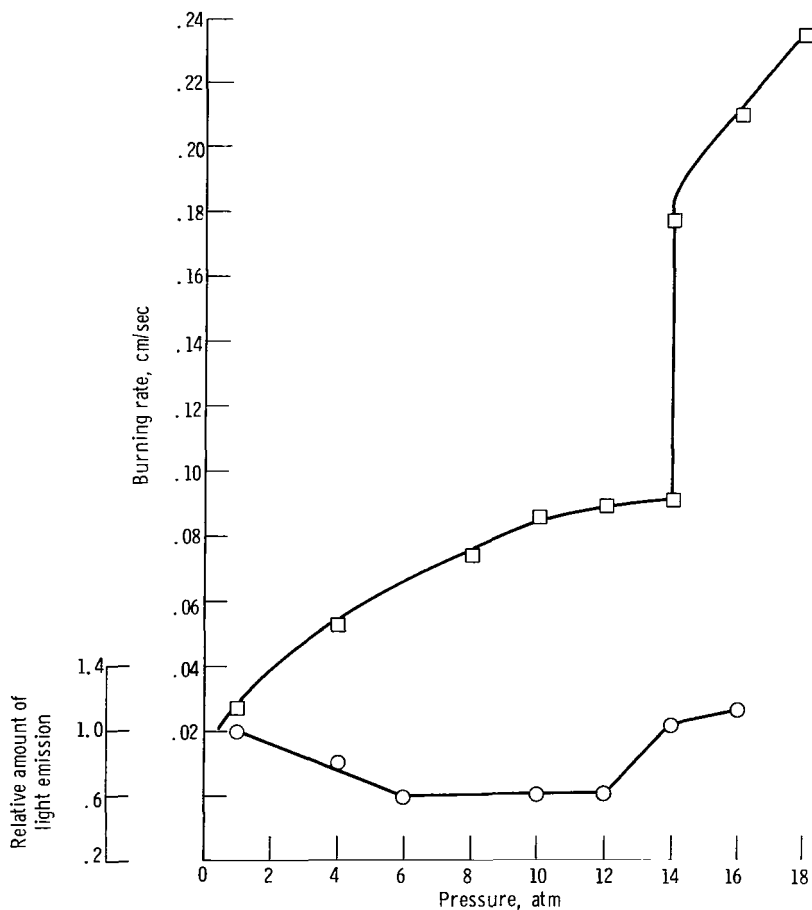


Figure 3. - Effect of pressure on burning rate and amount of light emission. Tube diameter, 5.6 millimeters.

indicate a change in the reaction. The results of the flame temperature measurements in a 5.6-millimeter-diameter tube are given in table I. It can be seen that, within the experimental error, the maximum gas temperature is not dependent on pressure or on burning rate. The latter can be seen particularly from the results obtained for a pressure of 14 atmospheres. The variation in the burning rate values indicates that the break in the curve is occurring at this pressure. A typical burning rate - pressure curve is shown in figure 3. Attempts to measure flame temperatures at higher pressures failed because the flame would go out when it reached the wire. The results are

mostly within 100° of the calculated value of 1480° K.

The amount of light emitted from the burning in a 5.6-millimeter-diameter tube was measured at various pressures. Typical data for relative amounts are given in table II and plotted in figure 3. As the pressure increases, the amount of emitted light decreases to a minimum at about 6 atmospheres, then tends to slowly increase, and then abruptly increases at 14 atmospheres. An abrupt increase in burning rate also occurs at 14 atmospheres.

The changes in flame size and shape that occur with the variation in light emission can be seen from the color photographs taken of the flame. Figure 4 shows a reproduction of those photographs. At 1 atmosphere the flame is roughly crescent shaped. It progressively thins in the pressure region from 4 to 14 atmospheres, but abruptly regains its crescent shape at 16 atmospheres. The burning rates are also included in the figure, and it can be seen that the rate abruptly increases between 14 and 16 atmospheres. If the flame is viewed from the top, it appears to cover the liquid surface at 1, 16, and 18 atmospheres, but only partially covers at the other pressures. At these intermediate pressures the flame appears as a ring close to the wall of the tube. When viewed from the side, a flame covering the liquid and following the contour of the surface would appear as a crescent, while one form-

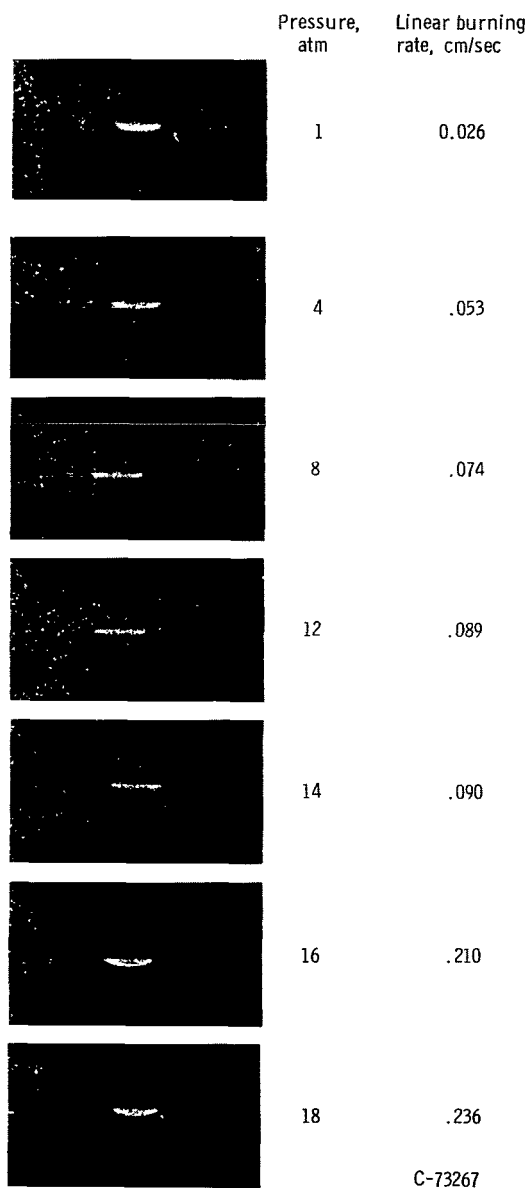


Figure 4. - Flame from hydrazine burning 5.6-millimeter-diameter tube.

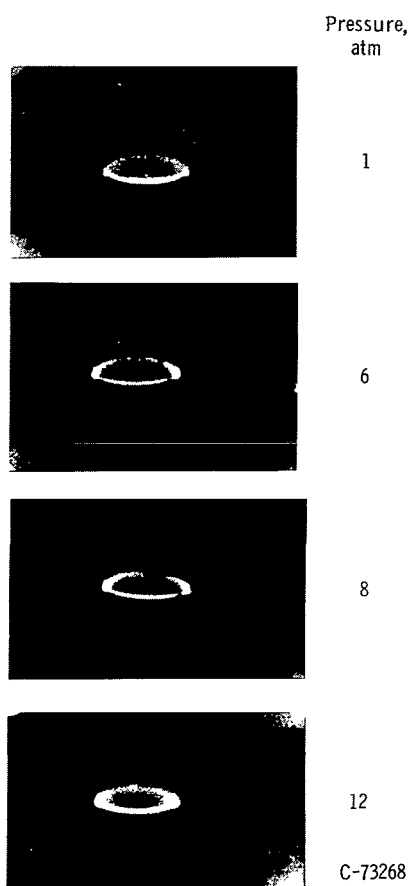


Figure 5. - Burning surface taken at 45° angle.
Tube diameter, 9.5 millimeters.

ing a ring would appear as a band or line. The pattern observed for burning in the 5.6-millimeter tube is also evident in the 9.5-millimeter-diameter tube. Figure 5 shows reproductions of color photographs of the top of the burning surface taken from about a 45° angle. The flame appears to cover the surface at 1 and 12 atmospheres with "ring-burning" in between. The break in the burning rate - pressure curve for 100.0 percent hydrazine in the 9.5-millimeter tube occurs at about 8 or 10 atmospheres (ref. 1).

Other photographs show that even though the burning of liquid hydrazine in glass tubes is ostensibly quite smooth and the surface maintains a uniform meniscus as it moves down the tube, the surface is mildly turbulent and appears to follow a spiral path down the tube. This seems to be true at all pressures.

Also, in tubes of large diameter, particularly in the 10- by 10-millimeter square tube, a crackling sound is heard during the burning. The noise level decreases as the pressure increases.

It appears that at least two modes of propagation are possible, as witnessed by the disparate burning rates at the points at which the breaks in the curves occur. Since the flame temperatures appear the same

throughout, at least up to 14 atmospheres in the 5.6-millimeter tube, and are independent of burning rate, it is reasonable to assume that the stoichiometry of the chemical reaction does not change. Therefore, there are no changes in mechanism that can be attributed to a change in the course of the overall reaction.

There was no new evidence obtained in the current study that helps to better define the mechanism at low pressures where the rate is approximately proportional to the square root of pressure. It was postulated in references 1 and 9 that the slower burning rates were due to a limitation by the evaporation rate of the liquid. This explanation was prompted in part by an observed discrepancy between the reaction rate for hydrazine consumption (0.036 mole/(cu cm)(sec)) calculated from a relation between burning velocity and quenching distance (ref. 9) and the reaction rate calculated from kinetic data (0.36 mole/(cu cm)(sec), ref. 10). However, it is found that if the reaction rate is calculated from the kinetic data using a flame temperature of 1500°K , which is appropriate for liquid hydrazine, rather than 1950°K as in reference 10, a value of 0.11 mole per cubic centimeter per second is obtained. This value differs by a factor of 3, rather than

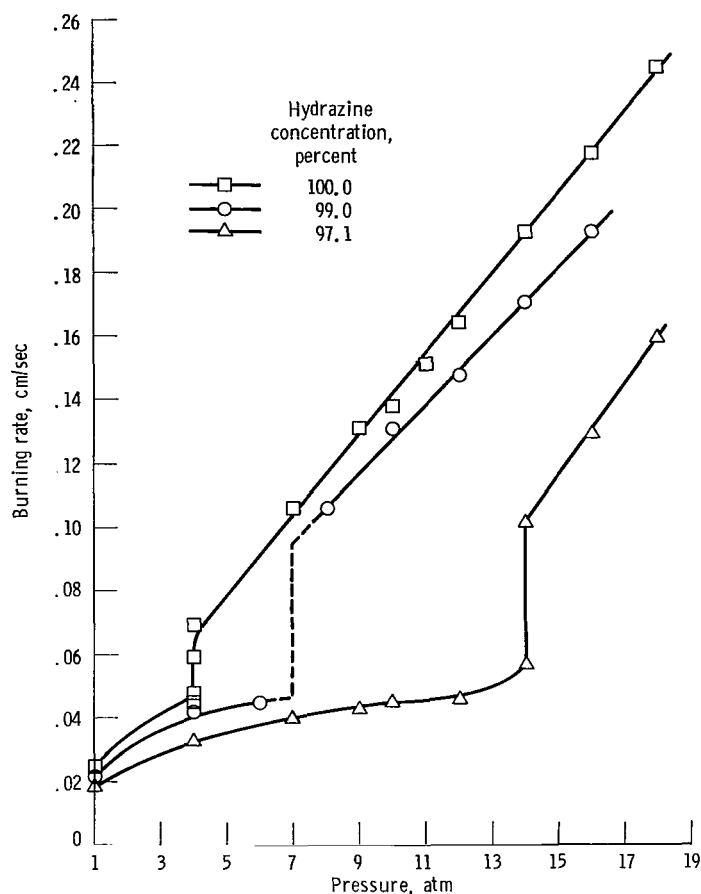


Figure 6. - Effect of pressure on burning rate of hydrazine-water solutions. Tube diameter, 12.7 millimeters.

of 10, from the burning velocity - quenching distance value. The better agreement weakens the argument favoring the evaporation rate limiting mechanism.

As to the pressure at which the break in rate occurs, some new burning rate data were obtained which complement that presented in reference 1. Additional data for 100.0 percent hydrazine in a 12.7-millimeter tube established a break at 4 atmospheres. New data were also obtained in the same sized tube for 99.0 percent hydrazine. These results are shown in figure 6 along with data for 97.1 percent hydrazine taken from the earlier report.

For a given concentration of hydrazine, 100.0 percent for example, the break pressure decreases with increasing tube size as shown in figure 7. This effect is qualitatively the same as the effect of tube size on the extinction pressure of hydrazine as reported in reference 7 and is also similar to the quenching behavior of burner flames. This suggests

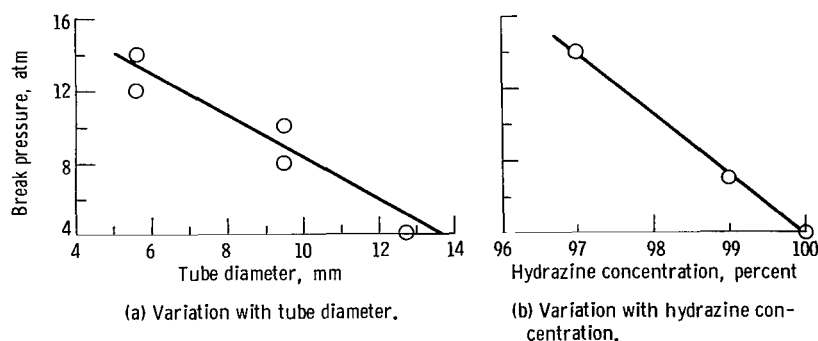


Figure 7. - Variation of break pressure.

that the break phenomena may be related to heat losses from flame to tube.

With a given tube diameter, the break pressure decreases with increasing hydrazine concentration as shown in figure 7. This again parallels the effect of concentration on extinction pressure reported in reference 7.

As to other observations, the most significant is in the changing appearance of the flame with changing pressure. As pressure is increased the flame recedes from the center of the burning strand to form a ring. Then, at the break pressure, the flame suddenly covers the surface. The flame also becomes less noisy as pressure increases. These observations suggest that physical and not kinetic factors change the apparent order of reaction.

CONCLUSIONS

The breaks in the burning rate - pressure curves for liquid hydrazine are not accompanied by any gross change in the smoothness of burning or any other readily visible distinguishing feature. Closer examination reveals, however, that there are changes in the size and shape of the flame, and the presence of a reduced amount of flame may be related to the lowered burning rate. It is concluded that physical factors are mainly responsible for the changes.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, November 27, 1964.

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